Report for 2005PR21B: Removal of Inorganic, Organic and Antimicrobials Contaminants from Aqueous Solutions by Waste Tire Crumb Rubber

Publications

- Other Publications:
  - Perales, O., Roman, F. and Arocha, M. ,2005, “Uso de Gomas Recicladas para Tratamiento de Efluentes”, Interview published in EL NUEVO DIA, one Puerto Rican main newspaper on June 20th, 2005.
  - Perales, O and Roman, F.,2005, “Removal of Heavy Metal Ions and Organic Solvents”, Invited Lecture at the AIDIS Conference,Isla Verde, Puerto Rico, September 30th, .
  - Perales, O., Roman, F. and Arocha, M., 2006, ‘The use of crumb rubber for the removal of organic solvents from aqueous Solutions’, Lecture presented at the University of Texas-El Paso on December 15, 2006.
  - 'Use of Recycled Crumb Rubber to Remove Organic Solvents from Aqueous Solutions’, Poster presentation at the 2nd Senior-ACS Conference, La Parguera, Puerto Rico, November 2005.
  - 'Crumb Rubber Evaluation as Absorbent for Tetracycline Antibiotic from Aqueous Solutions’. Poster presentation at the 26th Puerto Rico Interdisciplinary Scientific Meeting. Cayey, Puerto Rico, March 2006.
  - 'Use of Recycled Crumb Rubber to Remove Organic Solvents from Aqueous Solutions’ Poster presentation at the 26th Puerto Rico Interdisciplinary Scientific Meeting. Cayey, March 2006 and at the "12th Drinking Water Seminar", May 22-26, San Juan, Puerto Rico.

Report Follows

1. Project Summary

The present work was focused on the systematic evaluation of crumb rubber as a suitable material to remove inorganic and organic species from aqueous effluents through a low-cost and easy-to-scale technology based on the sorption properties of this waste material. Waste tires crumb rubber samples were kinfdly provided by REMA Inc, a Puerto Rican recycling company located in Caguas.

The capability of waste tires crumb rubber to remove organic solvents such as xylene, toluene and ethylbencene as well as antimicrobials of the type Tetracycline (TC) from aqueous solutions has been confirmed by batch wise sorption experiments at room temperature. As a complement to these studies, the adsorption of As(III) species was also evaluated. Preliminary studies with 5 ppm As solutions did not provide a clear evidence of adsorption. The As removal from mre dilute concentrations will be evaluated after installing the Atomic Absorption unit to be bought thanks to funds granted to the PIs by the Solid Waste Management Authority. This system is expected to be operational at the end of 2006.

The removal of organic solvents by waste tires crumb rubbers was a highly efficient and fast process. Sorption experiments verified that rubber particles (mesh 14-20 and mesh 30) were capable to remove more than 90% of the organic solvents in the first 30 minutes of contact at room temperature. For similar initial concentrations of the solvents, their removal efficiency and the corresponding rubber up-taking levels were dependent mainly on the solvent structure and the ratio weight crumb rubber/volume of solution. The solution pH did not affect significantly the removal efficiencies. For instance, up to 99, 95 and 77% of xylene, ethylbenzene and toluene respectively, were removed from starting 30 mg/L solutions. The solution pH was 6 and the rubber concentration 10g/L. The corresponding up-take capacities were 55, 48 and 24 mg/g rubber. The sorption capacity of crumb rubber was xylene > ethylbenzene > toluene, whereas higher crumb rubber concentration enhanced the corresponding up-taking levels.

Crumb rubber was also a very promising adsorbent for tetracycline (TC) from aqueous solutions. When 14-20 mesh crumb rubber was contacted with a 9.9 ppm TC solution, the net removal efficiency was 48.7 %. This value considered the observed degradation of the TC as suggested by the control tests. The removal efficiency was increased up to 58% when crumb rubber mesh 30 was used. Evidently, the higher specific surface of the smaller sizes (mesh 30) should have exposed a large concentration of adsorption sites, considered to be the carbon black nanoparticles embedded in the rubber matrix.

2. Statement of the Critical Problem

Protecting water bodies (surface, aquifers and coastal) from contamination is essential for health and safety. The limitations of conventional cleaning approaches become more evident when the contaminants are at very dilute concentrations as observed in effluents coming out from water treatment plants using conventional alkaline precipitation, or in ground waters polluted by hazardous species mobilized by leaching and/or percolation throughout soil substrates. Optional solvent extraction and ionic exchange systems are very expensive and they are tailored for high ion selectivity, which limits the removal of all contaminants through a single-step operation. In Puerto Rico, main problems of heavy metal pollution (mainly by Pb, Cu, Zn and Cd) have been reported in effluents from municipal wastewater, electroplating, metal finishing and printed circuit board manufacturing plants. In turn, the mercury pollution problem in Juncos and the presence of lead in some wells in Gurabo are examples of the aquifers contamination problem issue. The described situation is even more dramatic when the decontamination process deals with hazardous organic compounds, as those reported in some laundries and gas stations in Puerto Rico, where traditional precipitation and ionic exchange processes are not applicable at all. Antimicrobials such as Tetracycline (TCs) are of common veterinarian use to prevent epidemics and increase the weight gain in the animals. Very recently, the presence of these antimicrobials in water streams has been verified in Europe and the United States. This type of water pollution has raised environmental concerns based on the fact that up to 90% of the antibiotics fed to animals can be excreted in their active form. Therefore, the use of manure from antibiotic-treated animals as fertilizer and their wash-off by irrigation of rain precipitation should alter the microbial composition and ecology in the receptor soil as well as the quality of receptor water bodies. Diluted concentrations of antimicrobials can also selectively kill susceptible bacteria and favor the growth of resistant microorganisms, which in turn can become a pool of resistant genes. On a local basis, it has been detected that Puerto Rican tissues samples of cattle, calf and swine tissue samples contained excessive levels of agricultural residues. The violations were due to the presence of excessive antimicrobials in the animal tissue.

Accordingly, the development of a low-cost, environmental friendly and efficient cleaning process for effluents bearing inorganic and organic contaminants becomes indispensable.

About 4-million tires are discarded annually in Puerto Rico of them, approximately 800,000 tires are reused each year, and the remainder is land filled, stockpiled or illegally dumped. Land filling is a poor management option for scrap tires. Whole tires take up large amounts of valuable space in a landfill, coming up to surface shortly. New environmental regulations eliminate land filling as a disposal method, greatly increasing the environmental treat of scrap tires. Under this premises, the search of different alternatives to expand the re-use possibilities for scrap tires sounds justified.

Accordingly, the search of different alternatives to expand the re-use possibilities for scrap tires sounds justified. The present proposal is focused on the systematic evaluation of crumb rubber as a suitable material to remove inorganic, organic solvents and antimicrobials from aqueous effluents through a low-cost and easy-to-scale technology based on the sorption properties of this waste material. The remediation option addressed by this proposal is based on the presence of carbon black, zinc oxide, and sulfur in crumb rubber, with potential capability to absorb/adsorb and precipitate hazardous species from aqueous solution. This fact has been verified by preliminary results obtained in the first part of our work with Cu(II), Cd(II) and Pb(II) species. The sorbent will be kindly provided by Rubber Recycling and Manufacturing Corp., REMA, a Puerto Rican company that produces crumb rubber at different particle sizes from scrap tires.

3. Objectives of the Research (Phase-II):

This research work considered the following main objectives:

i. To optimize the sorption capability of crumb rubber for organic species from aqueous solutions. In order to maximize the up-takes and sorption rates of crumb rubber, alternatives for its activation (chemical) were also evaluated. Then, the sorption capability of granular crumb rubber for xylene, toluene and ethylbenzene was systematically investigated. Preliminary test of As(III) removal was also included.

ii. To asses the sorption capability of crumb rubber for antimicrobials (Tetracycline) from aqueous solutions.
iii. To asses the sorption rates and loading-capacity as a function of crumb rubber particles concentration, particle size and solution pH. It was considered the sorption behavior of the different target species under room temperature conditions in order to use the results in real effluents during the following stages of the research.

<u>Timeline of activities</u>

1) Physical and chemical stability of granular crumb rubber in aqueous media. The results of this part of the study were reported last year.
2) Chemical activation of crumb rubber for the removal of organic solvents.
2) Preliminary work on the adsorption of As(III).
3) Optimization for sorption of organic compounds: xylene, toluene and ethylbenzene.
4) Batch equilibrium and kinetic tests for sorption of tetracycline

4. Methods and Procedures

Granular crumb rubber, screened at different mesh sizes, will be kindly provided by REMA Corp. a tire rubber recycling company located in Caguas, Puerto Rico. It is estimated that a maximum of 4-kilograms of dry crumb rubber will be used for the sorption tests. This crumb rubber will be stored in appropriate containers.

4.1 <u>Experimental Procedures</u>
The basic set-up for the sorption tests includes temperature-controlled water shaker baths, stirrers, pH-meters, filtration and drying units. All quantitative analyses will be carried out in Dr. Felix Roman's laboratory. The term sorption here is used to include both *adsorption*, which refers to the retention of solutes by the surfaces of a solid material, and *absorption* which refers to the retention of the solutes within the polymeric matrix. Sorption processes result from physical, chemical and electrostatic interactions between the solid surfaces and the sorbate.

i. Sorption experiments
The following parameters were evaluated in batch equilibrium sorption experiments: average size of rubber particles, concentration of hazardous species, pH, and crumb rubber/solution w/w ratio. Sorption capability of crumb rubber will be evaluated for room-temperature conditions. To evaluate the role of carbon black on the different compounds sorption, a reference carbon black used by the rubber industry was tested to estimate its sorption capacity for TC. Synthetic solutions bearing the targeted species were prepared in distilled/dionized water. Solution pH was adjusted by suitable amounts of NaOH or HNO_3. Prepared solutions were then contacted with granular crumb rubber in Erlenmeyer flasks (inorganic species) immersed in a temperature-controlled water bath shaker. Samples and blanks were run in duplicate. After determining the pH of the solutions after the contact period, they will be filtered trough membrane filters and submitted for quantitative analyses by atomic absorption and/or ICP-OES techniques. In the sorption kinetic experiments, aliquots will be obtained at different time intervals and submitted for quantitative analyses of the residual species contents right after filtration. During the first step of the experimental work, the sorbent will be contacted with solutions containing single species.

The batch sorption tests for the organic compounds and antimicrobials followed a procedure similar to that for inorganic species. However, screw cap vials with Teflon-lined septa were used instead of common glass beakers and agitated on a hematological mixer. In order to minimize vapor loss and allow a suitable mixing, the head space in the vial after addition of the sorbent and sorbate, were kept at approximately 1 ml. In a typical run, 240 ml of 30 ppm of each organic solvent was contacted for 6 hours with crumb rubber 10, 5.0, 1.0, 0.5 y 0.1 g/L. Samples were withdrawn at different contact times using the micro-extraction technique in solid phase. Sorption tests were carried out by triplicate at inicial pH values of 1.5, 6.0 y 9.0.

iii. Activation experiments
Ten grams of crumb rubber were treated with 100 mL of 2.5, 5.0 and 10.0% nitric acid or 2.5% sodium hydroxide solutions for 24 hours. Crumb rubber was also treated under acid (HNO3, 5% v/v) and alkaline conditions (NaOH, 2.5% v/v). Each acid and alkaline treatment was for 24 hours at room temperature. After activation, crumb rubber samples were dried at room temperature conditions for 48 hours. Dried particles were then be contacted with solutions bearing organic contaminants. Thermal activation tests will be carried in the next stage of our project.

4.2 Quantitative analyses
Inductive Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) and Atomic Absorption Spectroscopy (AAS) are widely used in the determination of toxic metals in environmental matrices and will be used in this project for the quantitative evaluation of the sorption and desorption experiments. ICP-OES has multi-elemental capabilities, good sensitivity, high precision, accuracy, wide dynamic range and cost effectiveness. US EPA method 200.7 is based on the ICP-OES technique and used for the determination of heavy metals including As in aqueous solutions. The concentration of the organic compounds in the aqueous, gas and solid phases were determined by solid phase microextraction (SPME) and gas chromatography mass spectrometry. A Finnigan Gas Chromatography-Mass/Spectrometry/Mass Spectrometry system was used for quantitative analyses of organic solvents in aqueous solutions. In turn, EDTA has been used to increase extraction of higher concentrations of TCs in order to improve recovery by chelating metal ions in solution.

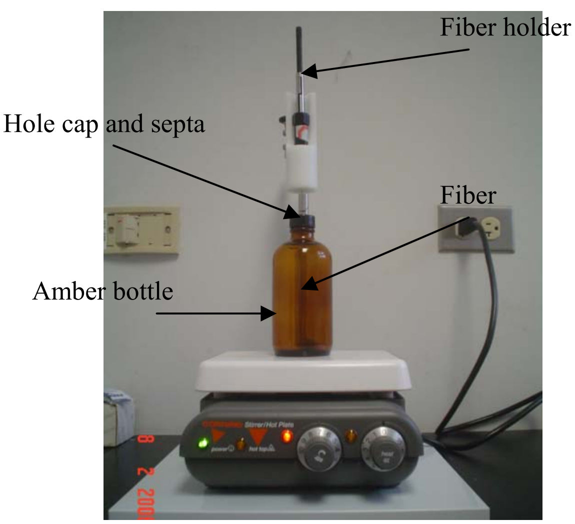


Figure 1. Solid Phase Microextraction set-up (left side) and the Gas Chromatography coupled with Mass Spectrometry Detector (right side)

5. The Sorbent: Waste Tires Crumb Rubber

Crumb rubber was provided by REMA Corporation a tire rubber recycling company located in Caguas, Puerto Rico.

Figure 2 REMA crumb rubber (Mesh 14 – 20). Size of tire rubber particles looks very homogeneous.

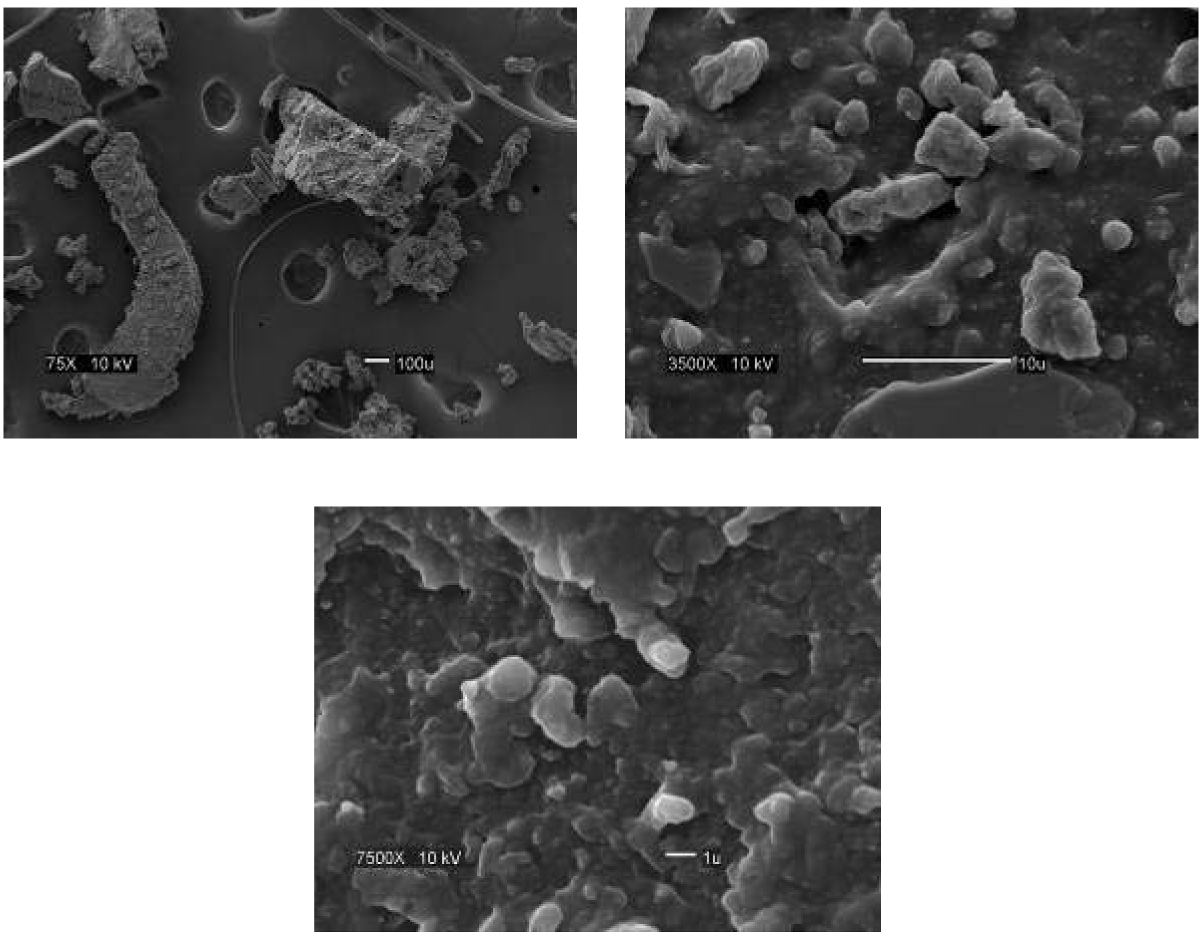


Figure 3 SEM pictures of crumb rubber. SEM analyses a very irregular surface roughness although with non observable porosity.

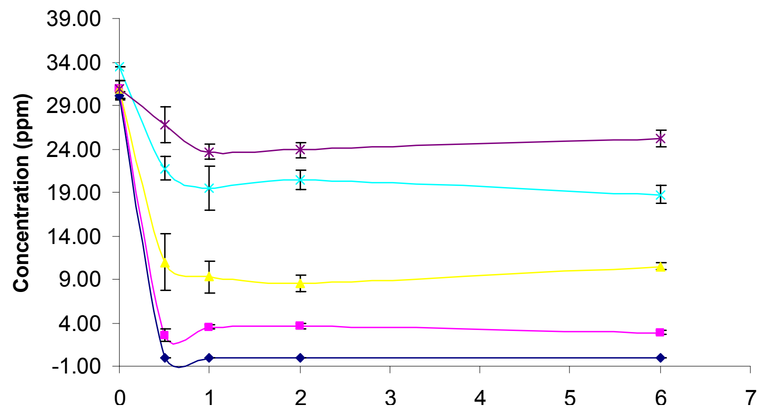
6. Principal findings and significance.

6.1 <u>Sorption of organic solvents</u>

Our recent work verified the very fast sorption of organic species by crumb rubber. Most of the organics were sorbed within the first 30 minutes of contact. Results of the sorption test at different pH values and concentrations of crumb rubber between 0.1 and 10 g/l, are summarized as follows. Quality controls (QC) of 30 ppm for each solvent were run in all experiments. Results were accepted if the error was below 20%. Ethylbenzene, toluene and xylene are non polar compounds which have low solubility in water (see table 1.1), and low concentrations of these compounds assure complete solubility. For that reason, we decided to keep constant the concentrations of analytes (30 ppm) and vary the concentrations of crumb rubber to get desired sorbent/solution ratios.

i. Removal of organic solvents at pH 6.0

a. XYLENE



b. TOLUENE

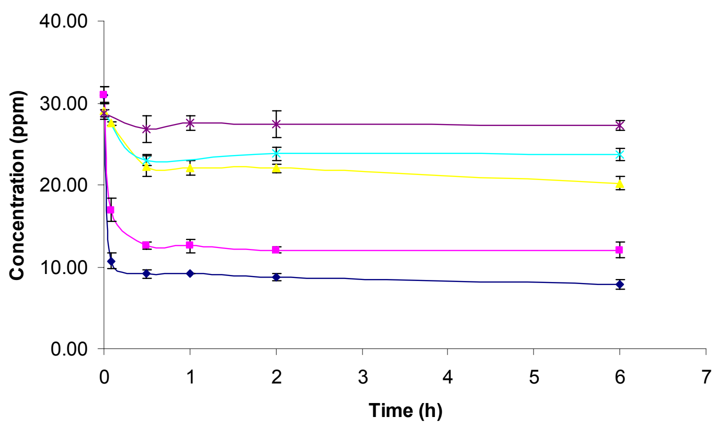
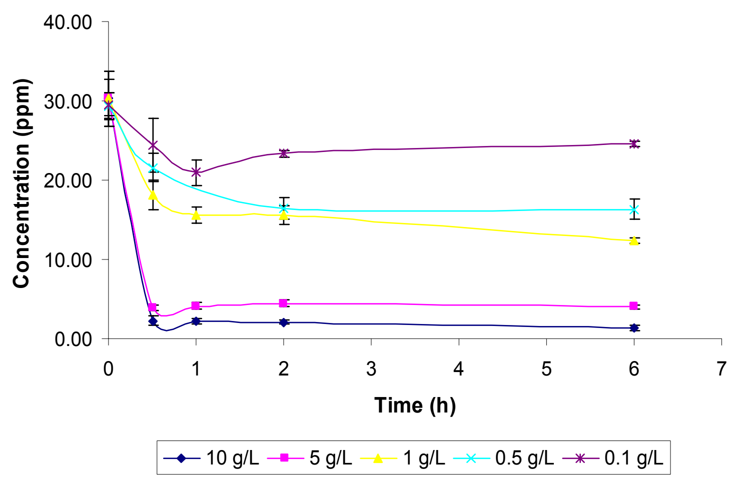


Figure 4. Sorption of ethylbenzene, toluene and xylene by 14-20 mesh crumb rubber. The concentration values in g/l correspond to the ratio weight crumb rubber/volume of solution. The initial concentration of organic solvent was 30 ppm and pH 6.0.

c. ETHYLBENZENE



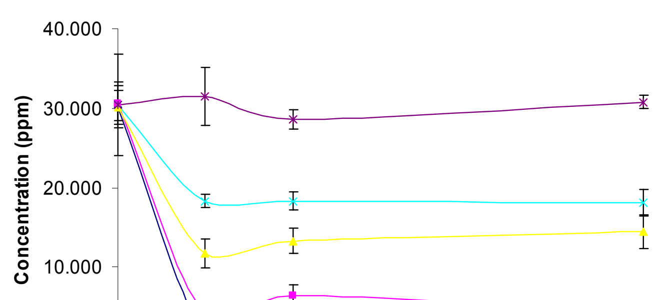
The capability o … clearly demonstrated by attained results. T …) was highly efficient and rapid. Most of the pollutants (above 90%) were removed in the first 30 minutes of contact time for suitable concentration of crumb rubber. These results are in good agreement with previous works (Guanasekara, 2000). Xylene was completely removed when 10 g/L of crumb rubber was used (which is the common adsorbent concentration used in the common practice). This high affinity of crumb rubber for xylene was followed by ethylbenzene and, lastly, toluene. Toluene was the highest solubility in water (515 mg/L); then, the partition between the crumb rubber and water is expected to be significantly different from the ones observed for xylene and ethylbenzene having solubilities of 200 mg/L and 152 mg/L, respectively. Xylene and ethylbenzene are more hydrophobic and, as expected, will be absorbed by the crumb rubber matrix more easily and rapid. Terminal concentrations exhibited a rising trend when the concentration of crumb rubber was less than 10 g/l. This behavior was expected because the lesser the amount of adsorbent, the lower the concentration of adsorption sites. At 0.1 g/L of crumb rubber, a minimum amount of pollutant was removed. Observed behavior is characteristic for complex sorbent like crumb rubber where all matrix is the host for active adsorption sites. As also shown in Figure 4, more than 40% of xylene and ethylbenzene were removed for crum rubber concentration as low as 0.5 g/l. The removal efficiency decreased down to 17 and 18% for ethylbenzene and xylene, respectively, when the crumb rubber concentration was 0.1 g/L (that means 100 times less crumb rubber than at 10 g/L).

The chemical composition and structure of crumb rubber is the key to understand its sorbent capability. Isoprene and butadiene are hydrocarbon chains present in crumb rubber that can interact with the alkyl groups of organic solvents. In turn, the presence of methyl groups in adjacent carbons in the structure of o-xylene can be considered as responsible for its adsorption due to a strong chemical affinity with hydrocarbon groups in the rubber matrix. This favorable chemical affinity between the methyl groups and the hydrocarbon ones in rubber can explain the very rapid and efficient removal of xylene by the crumb rubber. The second group in affinity is the ethyl group, which is longer than the methyl one. It could be the reason why ethylbenzene, host of ethyl groups, is removed by crumb rubber. The length of the ethyl group can be related to the comparatively les adsorption of ethylbenzene than toluene. Styrene is also a constituent of tire rubber; its aromatic ring will enable the interaction of styrene with all three organic solvents under study. On the other hand, the participation of carbon black in the sorption process can not be ruled out. Carbon black, 10-50 nm in diameter, exhibits a quite large superficial area and a well known adsorption capability.

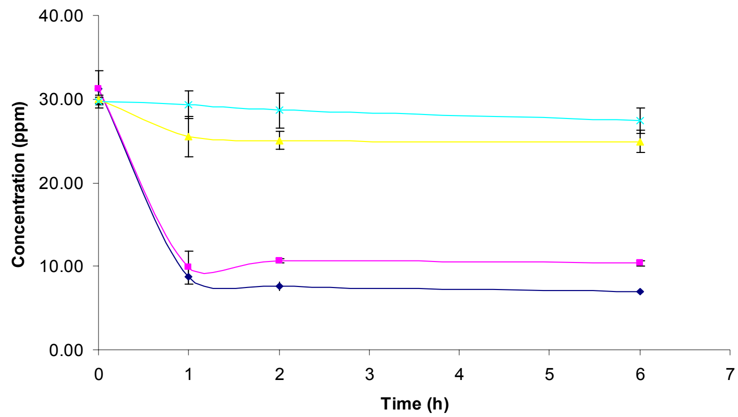
ii. Removal of organic solvents at pH 1.5

The trends in the removal efficiency did not exhibit major changes in comparison with those results at pH 6. In the first 60 minutes the majority of solvent was removed. Samples taken after 30 minutes of contact could not be analyzed because the system was not in equilibrium and the variability was high. It explains why the corresponding error bars for these conditions. A 10 g/L concentration of crumb rubber with an initial concentration of 30 ppm removed 95% of xylene at pH 1.5 which can still be considered excellent removal efficiency. The sorption behavior of toluene and xylene at 0.1 g/L crumb rubber was not considered due to the minimum sorption observed at low concentrations of crumb rubber.

a. XYLENE



b. TOLUENE



c. ETHYLBENZENE

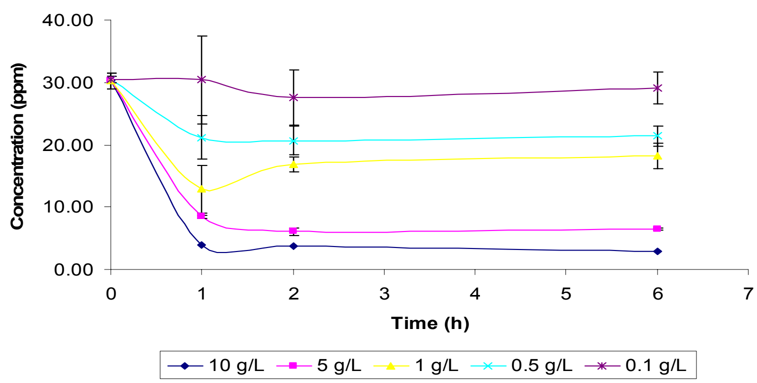


Figure 5. Sorption of ethylbenzene, toluene and xylene by 14-20 mesh crumb rubber. The concentration values in g/l correspond to the ratio weight crumb rubber/volume of solution. The initial concentration of organic solvent was 30 ppm and pH 1.5.

iii. Xylene removal at pH 9.0 and 5 g/L of crumb rubber

As evidenced by the data given in Figure 6, alkaline pHs did not affect the sorption behavior of xylene. As expected, the sorption behavior of organic solvents in presence of crumb rubber is practically a pH-independent process.

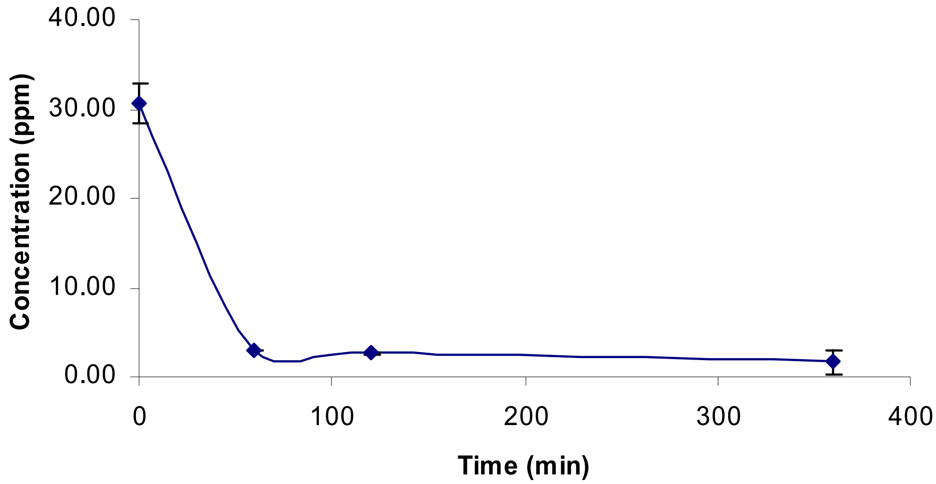


Figure 6. Sorption of xylene by 14-20 mesh crumb rubber (5 g/l). The initial concentration of organic solvent was 30 ppm and pH 9.0.

iv. Adsorption Isotherms

For most organic compounds the parameter 1/n is lest than 1 and values near 1 indicate rapidly removal at high concentration that decrease quickly when the concentration goes down. The other parameter is K_f and this indicates the adsorptive capacity or loading factor of the sorbent and a large value means high removal capacity. As the data in Tables 1 and 2 shows, the Langmuir isotherm better fitted the data for toluene and xylene at pH 6.0; and ethylbenzene and toluene at pH 1.5. In turn, Freundlich isotherms described better ethylbenzene at pH 6.0 and xylene at pH 1.5. Guanasekara et al. (2000) and Kim et al., (1997) worked with toluene and different kinds of rubber as sorbents. Both groups modeled their data using the Freundlich isotherm and found K_f values between 265-297 and 'n' values ranging from 0.993 to 0.991. In our work, we found 166.1 and 767.3 for K_f values; and 1.2683 and 0.6194, for n values, at pH 6.0 and 1.5 respectively. Accordingly, the crumb rubber we have used in the present research exhibited a better sorption capability.

TABLE 1 Parameters of linear, Freundlich and Langmuir isotherms for ethylbenzene, toluene and xylene at pH 6.0.

Compound	ISOTHERM							
	Linear		Freundlich			Langmuir		
	m	r^2	1/n	K_f	r^2	b	Q^o	r^2
Ethylbenzene	1935.8	0.9694	0.9728	1750.9	0.9697	0.04869	44247.8	0.9521
Toluene	581.1	0.9242	1.2683	166.1	0.9916	0.01372	10230.8	0.9987
Xylene	1963.4	0.9430	0.9913	1949.1	0.9779	0.04389	454545.5	0.9973

m : slope
i : intercept
r^2 : R square
n : Freundlich constant

K_f : Freundlich constant
b : Langmuir constant
Q^o : Maximum amount adsorbed

TABLE 2 Parameters of linear, Freundlich and Langmuir isotherms for ethylbenzene, toluene and xylene at pH 1.5.

	ISOTHERM							
Compound	Linear		Freundlich			Langmuir		
	M	r^2	1/n	K_f	r^2	b	Q^o	r^2
Ethylbenzene	767.4	0.9546	0.9155	946.6	0.9789	0.02327	41322.3	0.9833
Toluene	149.2	0.7976	0.6194	767.3	0.8975	0.05008	10101.0	0.9648
Xylene	1278.4	0.9577	0.874	1703.1	0.9746	0.05876	32051.3	0.9689

m : slope
i : intercept
r^2 : R square
n : Freundlich constant
K_f : Freundlich constant
b : Langmuir constant
Q^o : Maximum amount adsorbed

6.2 Chemical activation of crumb rubber

Our results suggested that the chemical activation of crumb rubber under acid, alkaline or acidic/alkaline conditions did not represent any improvement on the sorption capability of the crumb rubber in comparison with the non-activated one. Therefore, it seems advisable to consider the use of crumb rubber with no need for any acid/alkaline pre-treatment.

6.3 Sorption of tetracycline (TC). LC-MS/MS Chromatography Results

We used the selected reaction monitoring mode (SRM) and the internal standard method for the quantification of the concentration of TC in aqueous solutions. Crumb rubber and carbon black were used as sorbents. Prior to LC/MS quantitative analyzes, it was necessary the optimization of the measurement conditions. It included: chromatography separation, retention time, the ionization and detection mode of the ions, LOD, LOQ and Ion Trap Parameters. We took the MS and MS/MS spectrum of tetracycline (TC) and an internal standard (demeclocycline, DMC). TC showed the (M+H) ion in 445.10 m/z with product ions located at 427.10 and 410.20 m/z. The optimized chromatography conditions were: Mobile phase acetonitrile 40% deionized water, 1 % formic acid, pH 2.43; 0.40 mL/min

The LOD and LOQ of TC were estimated at 0.03 ppm and 0.10 ppm, respectively. Those values were 0.005 ppm and 0.05 ppm for DMC. MS spectra of DMC internal standard (IS) presented a (M+H) ion in 465.10 m/z and product ions in 448.08 and 430.00 m/z, due to fragmentation from parent ion (465.10 m/z). For MS quantification, the product ions in 410.20 and 427.17 m/z were monitoring to obtain the extract ion chromatogram (EIC) for TC. The corresponding calibration curve was adjusted to a quadratic polynomial. Presented results were obtained for 168 hours of contact time, pH 3.80 and initial TC concentration of 10.00 ppm. 14-20 mesh crumb rubber (CR), with and without acid washing (in HNO_3 2.5 %), and non-washed 30 mesh crumb rubber (CR) were used in the sorption experiments. For purposes of comparison, the sorption of TC in presence of carbon black was also carried out.

i. TC removal by crumb rubber mesh 14-20

Crumb rubber was capable to remove TC from aqueous solutions. Results are summarized in Figure 7. As seen, a drop in TC concentration from 9.85 down to 4.13 ppm when 14-20 mesh crumb rubber was used. After subtracting the degradation of TC, evidenced by the control samples, the net removal efficiency was 48.7%. In those tests with non-washed crumb rubber, the presence of Zn species (from ZnO in crumb rubber) should have competed with the crumb rubber polymeric material and/or carbon black as active adsorption sites for TC. Accordingly, TC molecules should have formed some complex with Zn sites in the crumb rubber at the earlier sorption stages. This mechanism could explain the larger removal efficiencies observed in the non-washed crumb rubber particles. This interpretation could also explain the abrupt drop in TC concentration at the beginning of the sorption process followed by an increase in its concentration, probably due to the release of the Zn-TC complex into the bulk solution. The stability of metal-TC complex is well documented in the scientific literature. Also, our ICP measurements have verified the continuous release of Zn ions in the course of the contact period. It also explains the rise in pH that would arise from the leaching of ZnO in the rubber. Further drop in TC concentration could be attributed to the Zn-TC complex adsorption by carbon black nanoparticles embedded in the rubber particles. It must be remarked that the solutions' pH at the end of the contact period differed from the initial value (3.80). For instance the final pH for the sorption test using mesh 14-20 crumb rubber without acidic treatment was 5.71. Evidently, this change in pH during contact period must have affected the removal capability of the crumb rubber. Future tests will be carried out under constant pH conditions to evaluate the real effect of this parameter on the sorption capability of crumb rubber.

When the sorption test was performed using acid washed mesh 14-20 crumb rubber, the terminal concentration was 6.02 ppm, which suggested a different absorption mechanism. In the acid washed crumb rubber, most of the Zn sites should have removed by the acid solution, limiting the sorption capability. It will also decrease the concentration of probable Zn-TC complexes in solution, which could have affected negatively the removal efficiency. Additional work must be carried out to clarify these probably mechanisms.

ii. TC removal by carbon black

The removal of TC by carbon black (N-330) was a highly efficient process. The concentration of carbon black in solution was equivalent to its concentration in the rubber particles (around 22% in weight). Therefore, 2.2 g/l of carbon black was considered equivalent to 10 g/l of crumb rubber. In these tests no change in the solution pHs during the contact period were noticeable. The TC removal varied between 97.80 and 100.00 %. Evidently, there is a great affinity between TC molecule and carbon black. On this basis, a major exposure of the carbon black nanoparticles to the TC solution should improve the removal efficiencies. It was attempted by using a crumb rubber mesh 30, which exhibit a particle size smaller than for mesh 14-20.

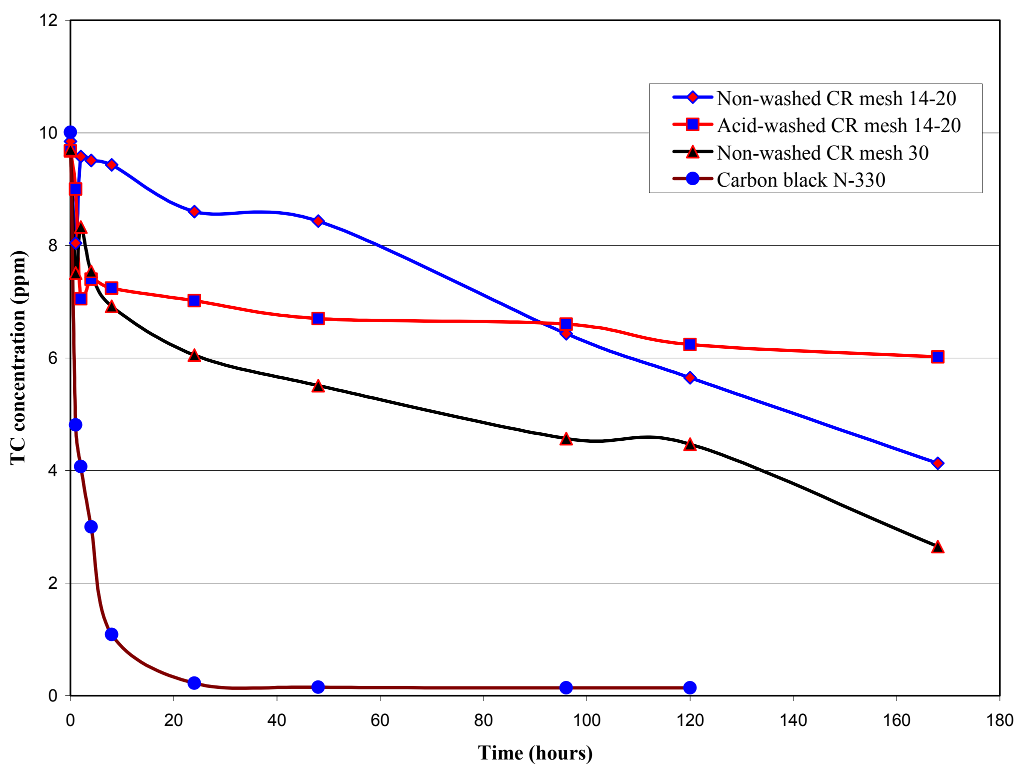


Figure 7. Variation in TC concentration with time for crumb rubber mesh 14-20, with and without acid washing, crumb rubber mesh 30 and carbon black (2.2 g/l). The concentration of crumb rubber was 10 g/l and the starting TC concentration 30ppm. Initial pH 3.8.

iii. TC removal by crumb rubber mesh 30

Almost 60% of the TC was removed by using crumb rubber mesh 30 (after subtracting the degradation of TC indicated by control samples). This result confirmed our previous hypothesis, i.e. the removal capability of crumb rubber will be improved by increasing the exposure of carbon black nanoparticles. Despite this favorable effect of rubber particle size on the sorption efficiency of TC, and from an industrial application viewpoint, the handling of small particles of crumb rubber (mesh 30, for instance) is not an easy task. To address this issue, future experimental work includes column tests to evaluate the capability of crumb rubber in a single and serial sorption stage(s).

6.4 Sorption of As(III)

The purpose of these 'screening-test' was to determine the sorption capability of crumb rubber in presence of As(III) ions species in aqueous phase. Preliminary tests with 5ppm of As did not show any clear evidence of actual adsorption of As by crumb rubber. A more detailed investigation will be undertaken using the AA unit to be purchased thanks to ADS funds granted to the PIs. The corresponding results will be discussed in the progressive reports to be presented in the next phase of our research.

7. Student Support

Section 104 Awards

Students	Base Grants
Undergraduate	1
Masters	3
Ph.D.	0

8. Achievements and Awards

- **Toyota Foundation** awarded to the research group the amount of $16,000 (01 year). The money is being used to cover stipends of graduate students participating in the project.
- **The Inter American Society of Sanitary Engineering and Environmental Sciences (AIDIS)** awarded the First Prize on Research to the work: ***"Remoción de BTEX por Partículas de Goma Recicladas en Soluciones Acuosas"***, presented by UPRM-PRWRERI last September 2005.
- Recently, the **Waste Management Authority (ADS) awarded $140,000** for the acquisition of major instrumental equipment. The grant is for instrumentation only. The instrumentation to be purchased will allow us to analyze concentration at the parts per billion (ppb) levels, as required for studies on mercury and arsenic (these two species are addressed in the present proposal as a complement to our studies on heavy metals). Legal considerations to be included in the contract have been completed. The final contract is expected to be signed by June 2006. Included equipment will be purchased and installed at UPRM before December 2006.
- Based on promising preliminary results, the research goals have been expanded to the evaluation of crumb rubber as potential sorbent for polyaromatic hydrocarbons (PAHs) in aqueous solutions (Phase-III of the present Project).

- The present research group involves: three faculties (02 from Materials Science and 01 from Environmental Chemistry) and three graduate students from the UPRM-Chemistry Department. The PIs plan to include at least a couple of undergrad students from Chemistry and/or Civil Engineering Departments.

Others:

- Although the HPLC/GC-MS methods for tetracycline were standardized, it works only for highly concentrated solutions (above 50ppm).
- In order to evaluate the sorption behavior at more dilute TC concentrations (<5ppm) a direct measurement by GC-MS must be considered.
- The atomic absorption unit to be purchased by ADS funding will allow us to analyze more dilute concentrations of As and Hg.